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Glass Formation, Properties and Structure of Soda-Yttria- Silicate Glasses

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GLASS FORMATION, PROPERTIES AND STRUCTURE OF SODA-YTTRIA-SILICATE GLASSES

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ABSTRACT

The glass-formation region of the soda-yttria-silicate system was determined. The glasses within this region were measured to have a density of 2.4 to 3.1 g/cm³, a refractive index of 1.50 to 1.60, a coefficient of thermal expansion of $7 \times 10^{-6}/^{\circ}\text{C}$ to $19 \times 10^{-6}/^{\circ}\text{C}$, softening temperatures between 500 and 780 $^{\circ}\text{C}$, and Vickers hardness values of 3.7 to 5.8 GPa. Aqueous chemical durability measurements were made on select glass compositions while infrared transmission spectra were used to investigate the glass structure and its effect on glass properties. A compositional region was identified which exhibited high thermal expansion, high softening temperatures and good chemical durability.

I. INTRODUCTION

Currently, only a limited number of glass systems have been reported that exhibit both high softening temperatures and high coefficients of thermal expansion (α_{CTE}). There is a demand for these types of glasses for use in coatings on superalloys and for glass-to-metal seals. Previous work conducted on yttria-silicate based glasses¹⁻³ have shown that these types of formulations exhibit the required properties for the above mentioned applications. However, only a limited amount of published data is available for many of these systems.⁴⁻⁶

Expansion in glass results from anharmonic vibrations of atoms whose amplitude increases as a function of temperature. These vibrations become larger in silicate glasses when asymmetry exists in the SiO_4 tetrahedra or upon the creation of nonbridging oxygen (NBO) atoms. NBO atoms form upon the addition of a modifier cation, the most common being members of the alkali series ions. In addition to increasing the oxygen content, these cation additions also force

some of the bridging oxygens to form NBO atoms. These NBO's are necessary to accommodate all of the oxygen atoms into the glass structure.

The degree to which the cation additions generate asymmetry in the structure follows the precept that the greater the ionic radius or smaller the field strength, the greater the effect each ion will have on the SiO_4 tetrahedra. The creation of these NBO groups disrupts the Si-O-Si network, which results in a lower softening temperature of the glass. As a result, the combination of both a high α_{CTE} and high softening temperature is increasingly difficult to attain in a glass.

The present investigation deals with the determination of the glass formation region in the soda-yttria-silica system. The glass density, refractive index, hardness, α_{CTE} , dilatometric softening temperature, and chemical durability as a function of composition within this region were measured. In addition, the structural groups in the glass forming compositions were analyzed by Fourier transform infrared (FT-IR) spectrometry. The determination of the glass-formation boundary was restricted to those compositions that melted at or below 1550 °C and which produced a glass when quenched in air. Correlations were also made between the measured properties and the glass structure.

II. EXPERIMENTAL PROCEDURE

(1) Sample Preparation

Glasses were prepared in 40 g batches using reagent grade Na_2CO_3 ,^{*} Y_2O_3 ,^{**} and ground SiO_2 . Each batch was melted in platinum-3% rhodium crucibles in a molybdenum-disilicide furnace between 1450 and 1550 °C for 3 hr to ensure homogeneity. Each melt was cast into a 4.0-cm by 1.5-cm by 1.5-cm bar on a steel plate. Volatilization losses were <1 wt %. Compositions that did not melt at or below 1550 °C were not investigated.

^{*}Morton Thiokol, Inc. Danvers, MA.

^{**}Kawecki Berylco Industries, Inc.

An approximation of the glass forming region along the $\text{Na}_2\text{O-SiO}_2$ binary composition was deduced from the $\text{Na}_2\text{O-SiO}_2$ phase diagram.⁷ Candidate glass compositions from the outer edge of the proposed binary glass-formation region were melted and cast on to the steel plate to determine if a glass would form. If a melt could not be obtained as a glass after casting up to 10 times, a new composition was chosen along a line drawn approximately normal to the tangent of the glass-formation boundary (Fig. 1). Compositional changes were made at 1 wt % intervals once significantly large glassy regions began to form. The same technique was then used for compositions containing yttria, starting with those closest to the soda-silica binary and working to the higher yttria content compositions. The absence of crystalline phases in the cast bars was confirmed by viewing the bars under transmitted light at 200X. Samples were also examined by scanning electron microscopy (SEM) using back-scattered electrons (BSE) to determine if there was any detectable phase separation.

Once the glass-formation region was determined, additional glasses within the boundary region were prepared such that the mole fraction of one of the oxides remained constant (Fig. 1). This resulted in three compositional series: (1) $(30-x)\text{Na}_2\text{O} \cdot x\text{Y}_2\text{O}_3 \cdot 70\text{SiO}_2$, (2) $x\text{Na}_2\text{O} \cdot 5\text{Y}_2\text{O}_3 \cdot (95-x)\text{SiO}_2$, and (3) $25\text{Na}_2\text{O} \cdot (75-x)\text{Y}_2\text{O}_3 \cdot x\text{SiO}_2$, where x varied from 0 to 12.5 for series (1), from 15 to 40 for series (2), and from 62.5 to 75 for series (3). Trends in the glass properties as a function of substituting one component for another could then be measured. Each glass was annealed between 450 and 700 °C until no birefringence was visible when viewed with polarized light. The annealed glasses were then used for all subsequent measurements.

(2) Property Measurements

Glass densities were measured with a precision of $\pm 0.015 \text{ g/cm}^3$ by the Archimedes technique using water as the immersion liquid. Measurements were made at $22 \pm 1 \text{ }^\circ\text{C}$ using a density of 0.998 g/cm^3 for the water. Refractive indices were measured with a precision of ± 0.001 at a wavelength of 488.4 nm (sodium absorption line, n_D) using the Becke line technique.

Vickers hardness numbers (H_v) were reported from the average of five separate indentations. These indentations were made with a diamond indenter using a 50 g load on glass bars that had been polished with 1 μm alumina powder. H_v was calculated using the equation:

$$H_v = 1854.4 P/d^2 \quad (1)$$

where H_v has the unit's kilogram per square millimeter (subsequently converted to gigapascals), P is the load in grams, and d is the average length of the diamond indentation diagonal in micrometers. The estimated error is ± 0.1 GPa.

The α_{CTE} of the glass bars (25.4 mm in length) was measured with a horizontal alumina dilatometer at a heating rate of 3 K/min. The average value for α_{CTE} was determined from the slope of the expansion curve between 150 and 450 $^{\circ}\text{C}$. The dilatometric softening temperature (T_D), defined as the temperature at which the maximum in the expansion curve occurs, is reported instead of the glass transition temperature due to the lack of any significant change in slope of the expansion curves before T_D . The thermal expansion coefficient was accurate to $\pm 0.2 \times 10^{-6}/^{\circ}\text{C}$ while T_D is reproducible to ± 5 $^{\circ}\text{C}$.

Chemical durability for selected compositions was measured at two temperatures, 75 and 90 $^{\circ}\text{C}$, using approximately 1 cm^3 samples cut from bulk specimens and polished with 600 grit SiC paper. Each sample was placed in a plastic vial filled with 20 ml of preheated, de-ionized water. The vials were held in a temperature controlled oven ($\pm 1^{\circ}\text{C}$) for 30 min intervals for a total of 20 hr. Weight changes were measured by thoroughly drying and then weighing each sample after every interval. The de-ionized water in each vial was also changed during this period.

Infrared (IR) transmission spectra were obtained using pellets prepared by mixing 2.5 mg of -25 μm glass powder with 300 mg of KBr and pressing at approximately 138 MPa in a vacuum die. The IR spectra were obtained in the mid-IR from 4000 cm^{-1} to 350 cm^{-1} .

III. RESULTS AND DISCUSSION

(1) Property Measurements

A large glass-formation region was found in the soda-yttria-silicate system for compositions that melted at or below 1550 °C, as shown in Fig. 1. The shape and size closely agreed with previous work conducted by Alexander and Riley.⁵ The melting temperature of compositions along the silica rich region was greater than the 1550 °C limit of this study. These compositions may still form glasses but were not examined in the present investigation. The region of composition with melting temperatures greater than 1550 °C is depicted as a dashed line on the glass-formation boundary in Fig. 1. Glass-formation was limited to those compositions with less than 15 mol % yttria. All the glass forming compositions produced optically transparent glasses with no coloration. No phase separation was detected visibly or with BSE imaging using the SEM.

Density and n_D measurements for these glasses are shown in Figs. 2 and 3, respectively. The density of the glasses increased as yttria replaced either soda or silica, with the replacement of the silica creating a slightly larger effect. This is consistent with the molecular weights of the three components, with yttria being much heavier (225.8 g/mol) than silica (60.1 g/mol) or soda (62.0 g/mol). A small increase in density was also measured for soda replacing silica at constant yttria. This increase is greater than what might be expected from the small difference between the molecular weights of the two components. It can be explained by the difference between the glass structural roles of silicon in comparison to sodium ions. Silicon combines with oxygen atoms to create the glass network through interconnected SiO_4 tetrahedra while sodium occupies interstitial positions in the glass structure. By occupying interstitial sites within the glass structure, sodium has a greater effect on the density of the glass than what would be predicted from simple molecular weight considerations.

Values for n_D followed the same compositional trends observed for density, as expected. The molar refractivity of a glass is a function of the electron density of the ions present and the polarizability of the oxygen ions. The oxygen ion polarizability is related to the field strength of the surrounding cations. The cation field strength, in turn, is inversely related to its ionic radius. Yttria, with less firmly bound outer electrons and small field strength, increased the n_D as it replaced both silica and soda in the glass structure. An increase in n_D was also measured as soda replaced silica with constant yttria. The replacement of silica with soda results in an increased number of weak bonds between the oxygen and sodium ions. This enables the oxygen atoms to become more easily polarized and thus contributes to an increase in n_D .

The α_{CTE} of these glasses is primarily controlled by the soda content, as shown in Fig. 4. A sharp increase in α_{CTE} occurs upon the replacement of silica or yttria with soda. This results from the combined effect of the increased number of NBO atoms and from the higher degree of asymmetry in the SiO_4 tetrahedra. A moderate increase was also measured on the replacement of yttria by silica at constant soda content. This is somewhat unexpected since by increasing the silica content, the Na_2O/SiO_2 ratio is decreasing, which should lead to decreasing α_{CTE} values. One possible explanation of this is that yttrium is taking on a network role in the glass. When yttria (O/Y ratio of 3:2) is replaced by silica (O/Si ratio of 2:1), the ratio of oxygen to silicon atoms increases. This results in an increased number of NBO atoms that increases α_{CTE} . The large radius of the yttrium ion also increases its tendency towards a higher oxygen coordination that will cause further increases in α_{CTE} .

Rapid increases in T_D (Fig. 5) occurred when yttria replaced either soda or silica in the glass structure. Moderate decreases in T_D occurred when soda replaced silica. A maximum in T_D occurred for the constant soda series at 65 mol % silica, corresponding to a softening temperature of 735 °C. Generally, T_D decreases when the number of NBO ions increases and/or when atoms with strong M-O bond strengths are replaced by a species with a weaker

M-O bond strength. Soda can generate both of these effects as it replaces either silica or yttria. The decrease in T_D for the replacement of yttria by silica supports the conclusion that the number of NBO ions is increasing. This can be the result of yttria additions assuming an intermediate role in the glass structure.

Values for H_v increased rapidly when yttria replaced soda or silica in the glass structure (Fig. 6). Moderate decreases in H_v were also measured when soda replaced silica at constant yttria content. These changes in H_v match the compositional trends observed for T_D . Similar to T_D , H_v generally decreases when the number of NBO atoms decreases or upon the reduction in cation-oxygen bond strength. As discussed previously, this occurs when yttria is replaced by soda or silica and when soda replaces silica.

A wide range of aqueous chemical durability data was obtained for the soda-yttria-silica system, which are given in Table I. Glasses with the lowest weight losses were high in both silica and yttria while the highest weight losses were the binary soda-silicates. Chemical durability was found to be primarily controlled by the yttria content, with weight losses changing substantially for yttria additions as low as 3 mol % (glasses 3 and 4, Table I).

(2) Infrared Spectra

By observing changes in each absorption band as a function of glass composition, variations in the nature of the glass structure may be examined and correlated with the effect on glass properties. Figure 7 shows typical mid-IR spectra of seven glasses of different molecular composition. No IR absorption bands were observed in the glasses between 4000 and 1200 cm^{-1} . The spectrum for each composition is dominated by a broad absorption band centered between 1010 and 1065 cm^{-1} , which corresponds to Si-O-Si stretching vibrations involving the displacement of oxygen atoms. A second band, centered between 935 and 970 cm^{-1} and overlapping the first band, corresponds to the stretching vibrations of O-Si and O-Si-O NBO groups. The smaller absorption band between 740 and 770 cm^{-1} coincides to the bond stretching

modes primarily involving displacement of silicon. Finally, the band between 520 and 535 cm^{-1} corresponds to a Si-O bending mode.^{8,9}

When soda replaced silica at constant yttria (glasses A, B, and C, Fig. 7), the Si-O-Si band at 1040 cm^{-1} broadened and the minimum shifted to lower wavenumbers. In addition, a strong NBO band appeared at 936 cm^{-1} , signifying that the replacement of silica by soda disrupted the SiO_4 tetrahedral network resulting in the formation of NBO atoms in the structure. This is reflected in the higher α_{CTE} values, lower T_D and lower H_v values observed for these compositions. Since the sodium atoms are occupying interstitial positions in the glass structure, increases in density are also observed. A similar trend can be observed in the bending mode band, which initially appears at 770 cm^{-1} and shifts to 740 cm^{-1} while becoming much less pronounced upon the addition of soda. A small shift to higher wavenumbers was also measured for the band centered at 530 cm^{-1} , which is consistent for the type of structural changes occurring in the glass.⁸

When yttria replaced soda at constant silica, a different effect was observed. Glass D (Fig. 7), which contained no yttria, has a distinct NBO absorption band at 972 cm^{-1} and a Si-O-Si stretching band at 1060 cm^{-1} . Upon addition of yttria, the Si-O-Si band shifted downward in wavenumber and overlapped with the NBO band to form a single band centered at 1013 cm^{-1} . Both bands decreased in intensity, however the decrease is slightly greater in the NBO band. With further addition of yttria, the NBO band decreased further in intensity which resulted in the combined band minimum shifting to a slightly higher wavenumber (1018 cm^{-1}). Meanwhile, the bands centered at 760 and 525 cm^{-1} both decreased in intensity and shifted to slightly higher wavenumbers. This is an indication that the number of NBO's has decreased. This would result if yttria, in addition to occupying interstitial positions in the glass structure, is serving as an intermediate in the glass network. These types of structural changes would provide an explanation for the observed increases in T_D and H_v and the decrease in α_{CTE} .

As silica replaced yttria at constant soda content (glasses G, H, and I, Fig. 7), a similar trend to the one found in the first series of glasses was observed. Glass G shows a strong Si-O-Si band at 1028 cm^{-1} , an intermediate NBO band at 936 cm^{-1} and a low intensity 740 cm^{-1} band that is followed by a relatively strong band at 535 cm^{-1} . With the addition of silica, the first Si-O-Si band shifted downward in wavenumbers and overlapped with the NBO band to form a single band centered at 1013 cm^{-1} . Upon addition of more silica this band became broader and nearly flat along the minimum. This suggests that while the Si-O-Si band minimum is increasing in wavenumber, the NBO band is increasing in intensity as more NBO atoms form. With the decrease in the yttria content, the Si-O-Si stretching band at 765 cm^{-1} increased in intensity as yttrium was removed from the glass structure. This resulted in an upward shift in wavenumber of this band while the band at 535 cm^{-1} shifted down to 520 cm^{-1} . These structural changes contribute to the increase in the α_{CTE} and decrease in H_v and T_D observed in the glass property measurements.

CONCLUSIONS

A region of glass composition centered on the $25\text{Na}_2\text{O} \cdot 5\text{Y}_2\text{O}_3 \cdot 70\text{SiO}_2$ was identified as having both a high α_{CTE} and T_D . In addition, compositions in this region exhibited good chemical durability. Given these properties, a portion of these glasses meet the requirements necessary to make suitable starting compositions for high temperature coatings for superalloys and for glass-to-metal seals.

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TABLE I. - AQUEOUS CHEMICAL DURABILITY WEIGHT CHANGE
DATA

[Weight change in aqueous solution, grams per square centimeter.]

Number	Glass composition	75 °C		90 °C	
		10 hr	20 hr	10 hr	20 hr
1	$32\text{Na}_2\text{O} \cdot 3\text{Y}_2\text{O}_3 \cdot 65\text{SiO}_2$	-0.0019	-0.0024	-0.0285	-0.0507
2	$15\text{Na}_2\text{O} \cdot 3\text{Y}_2\text{O}_3 \cdot 82\text{SiO}_2$	-.0002	-.0005	-.0007	-.0144
3	$27\text{Na}_2\text{O} \cdot 5\text{Y}_2\text{O}_3 \cdot 68\text{SiO}_2$	-.0004	-.0007	-.0255	-.0468
4	$30\text{Na}_2\text{O} \cdot 2\text{Y}_2\text{O}_3 \cdot 68\text{SiO}_2$	-.4756	-10.843	-8.64	-15.31
5	$18\text{Na}_2\text{O} \cdot 8\text{Y}_2\text{O}_3 \cdot 74\text{SiO}_2$	-.0002	-.0003	-.0130	-.0142
6	$21\text{Na}_2\text{O} \cdot 3\text{Y}_2\text{O}_3 \cdot 76\text{SiO}_2$	-.0003	-.0004	-.0217	-.0276
7	$35\text{Na}_2\text{O} \cdot 6\text{Y}_2\text{O}_3 \cdot 60\text{SiO}_2$	-.0047	-.0258	-.1586	-.8659

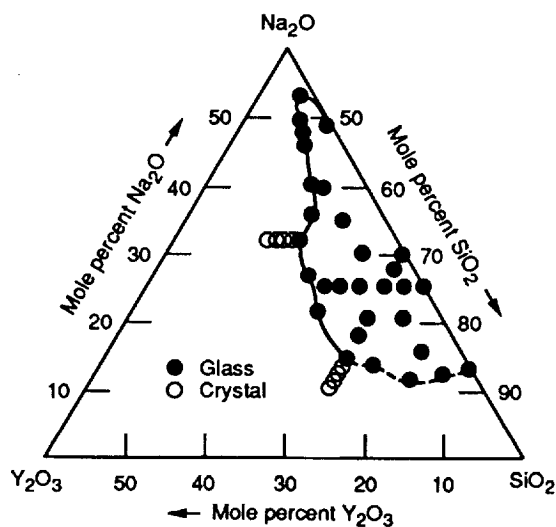


Figure 1.—Glass-forming region in the soda-yttria-silica system. Boundary of the glass forming region is indicated by the solid line; the dashed line is the 1550 °C temperature limit above which compositions were not melted. Glass compositions on which property measurements were conducted are shown as [●] within the glass-formation region. Compositions that contained crystalline regions after casting are shown as [○].

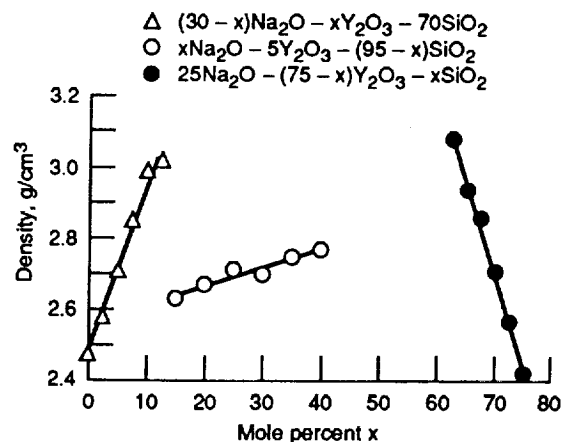


Figure 2.—Effect of glass composition on density.

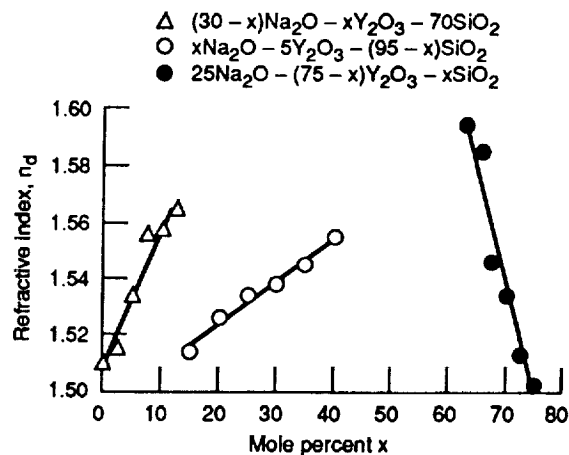


Figure 3.—Effect of glass composition on refractive index.

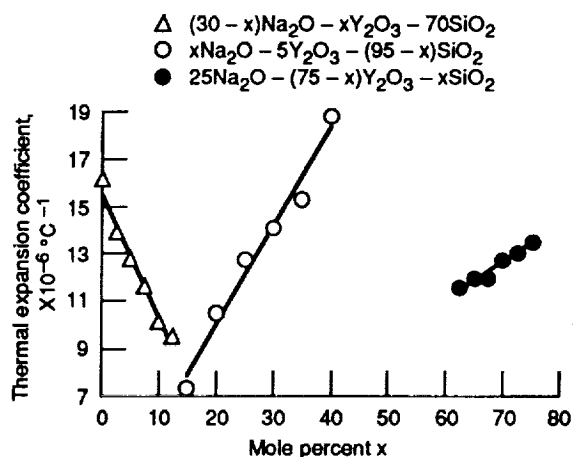


Figure 4.—Coefficient of thermal expansion as a function of composition.

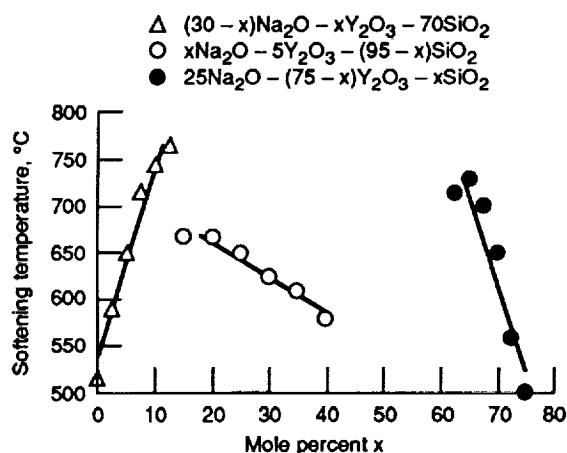


Figure 5.—Effect of composition on the dilatometric softening temperature.

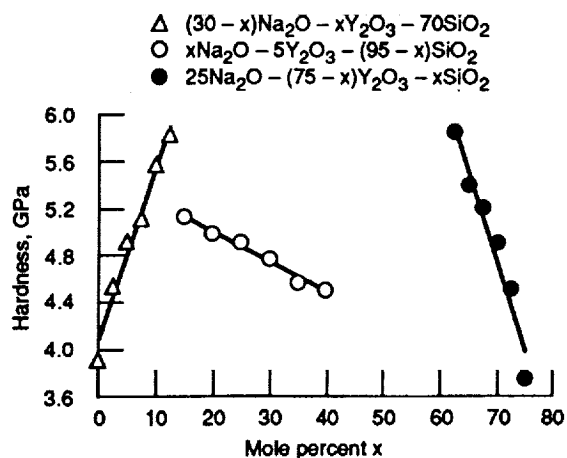


Figure 6.—Hardness as a function of composition.

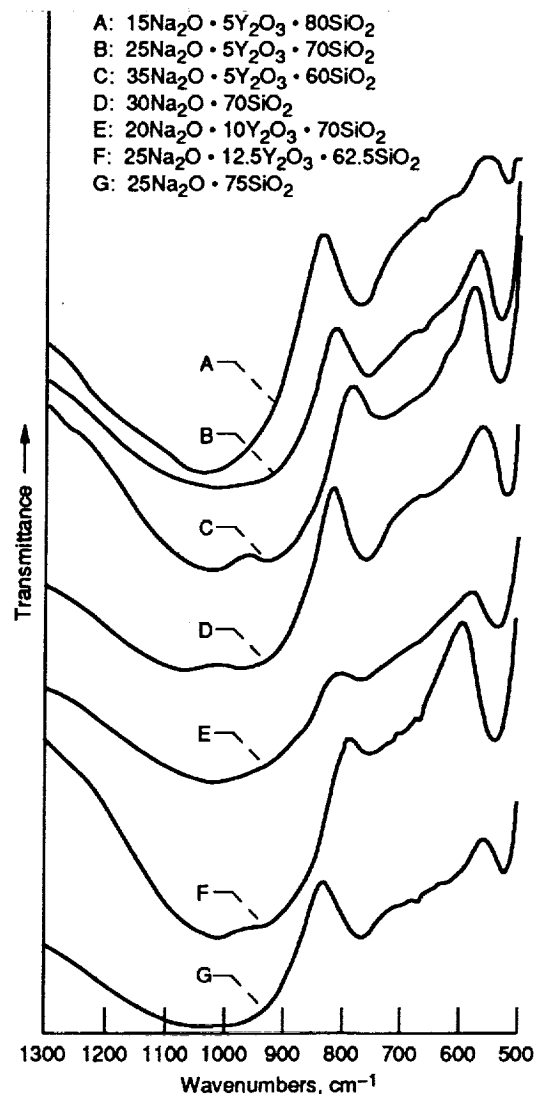


Figure 7.—IR spectra for 7 different glass composition as a function of wave number.



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